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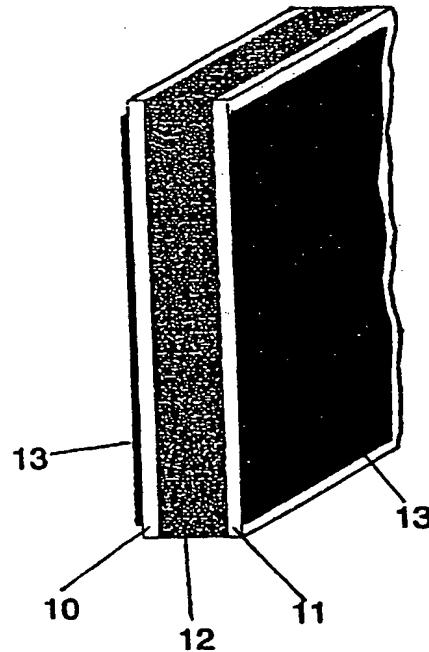
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[Continued on next page]

(54) Title: MAGNESIUM-BASED PRIMARY (NON-RECHARGEABLE) AND SECONDARY (RECHARGEABLE) BATTERIES

(57) Abstract: The batteries described herein are of the type comprising at least one anode, at least one cathode and at least one electrolyte, and current collectors, in which at least the anode is magnesium-based, and optionally also the cathode and the electrolyte contain magnesium. Assembly of the batteries involves the preparation of the individual components and the interposition of a thin layer of electrolyte between the magnesium-based anode and the cathode.



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MAGNESIUM-BASED PRIMARY (NON-RECHARGEABLE) AND SECONDARY (RECHARGEABLE) BATTERIES

Scope of the invention

The present invention regards primary (i.e., non-rechargeable) and secondary (i.e., rechargeable) batteries in which at least the anode contains magnesium, and optionally also the electrolyte and cathode contain magnesium, as well as methods for making said batteries.

Prior art

As is known, the enormous and rapid development of digital electronics that has taken place in recent years has enabled the creation of a large number of new portable devices, such as computers, cellphones, videocameras, etc. These devices are almost exclusively equipped with storage batteries built according to a single technology; namely nickel-cadmium (Ni-Cd) batteries.

The need to produce ever smaller and lighter portable devices, together with the need for long operating autonomy of these devices, has pushed numerous private firms operating in the sector, as well as public research bodies, to carry out research aimed at developing new technologies capable of meeting the requirements referred to above.

In the late eighties and early nineties, two new types of batteries appeared on the market: nickel-metal hydride (Ni-MH) and lithium-ion (Li-ion) batteries.

In just a few years, the performance of batteries produced using these technologies has improved considerably, to the extent that today the performance of these batteries is superior to that of nickel-cadmium batteries.

A further advantage of the batteries produced using these new technologies is the absence of cadmium, which, since it is a heavy metal, has quite a serious detrimental impact on the environment.

As is known, lithium-ion batteries are, in energy terms, still the most promising ones, but their production cost is relatively high. However, if the cost per cycle of these systems is considered, it may be noted that they become competitive as compared to the more economical nickel-cadmium batteries. On the basis of the technical characteristics, environmental impact, and cost per cycle, a considerable growth is expected for the lithium-ion system on the world market.

On the other hand, nickel-metal hydride batteries are likely to have a more modest growth, whilst it is estimated that nickel-cadmium batteries are unlikely to maintain their current production levels.

The international scenario witnesses a concentration of the majority of production 5 in the sector of lithium-ion batteries, which are an evolution of lithium systems.

Primary lithium batteries, which are widely used in calculators, clocks and watches, cardiac pacemakers, etc., are made with a lithium anode and a cathode made of transition metal oxide (e.g., MnO_2). Thanks to the high electrochemical potential supplied by the lithium anode, these batteries provide high cell voltages, 10 and consequently also high energy densities.

However, these systems are not reversible, or at the most are usable for just a few cycles.

The idea of exploiting lithium to make secondary batteries has given rise to a first technology known as lithium-polymer (Li-polymer) technology. This method, which 15 exploits metallic lithium for making the anode, presents, however, serious difficulties in terms of reversibility. In fact, during the recharging phase, dendritic deposits are formed on the surface of the anode, which are the result of the reaction of the lithium with the organic polymeric electrolyte and are responsible for the fast deterioration of this type of battery.

20 At best, the number of cycles obtained using systems of this type thus amounts to just a few dozens or hundreds.

On the other hand, the reactivity of the lithium in regard to the polymeric electrolyte may also become a cause of serious problems of safety in the operating phase of the battery itself.

25 The next step in the development of these devices was that of the introduction of the so-called lithium-ion or rocking-chair technology, which is based on solutions that tend to solve the problem of formation of dendrites on the lithium anode by replacing the lithium with composite materials capable of intercalating Li^+ in their structure via insertion reactions.

30 In recent years, it has been possible to produce anodes based on carbon with properties of intercalation. Certain carbons with a regular structure (turbostatic or graphitizable) or with a highly crystalline structure (natural or synthetic graphites)

can in fact intercalate the Li^+ ion in their layers in a reversible manner, thus giving rise to complexes of the Li_xC_6 type.

Other lithium-ion batteries are provided with an intercalated titanium disulphide-based (Li_xTiS_2) anode. The latter has a behaviour similar to that of a carbon electrode.

Usually the cathode is instead made using oxides of lithium and transition metals, among which the most widely used up to now is lithium cobaltate (LiCoO_2), which, for reasons of cost, availability, and toxicity, tends to be replaced by lithium nickelate (LiNiO_2) or lithium manganate (LiMnO_4).

The number of cycles achievable using the rocking-chair technology reaches one thousand.

Usually, in these systems the electrolyte consists of an organic polymer with solvent properties, which is rendered ionic-conductive by being doped with special lithium salts (e.g., LiPF_6 , LiClO_4 , etc.).

Notwithstanding the fact that the above-mentioned technological advances tend to solve the problems linked to the use of lithium on account of the high reactivity of this element, and in particular the main problem linked to the formation of dendrites on the anode, research for a complete solution to these problems is still very much in progress. The problem of the formation of dendrites has not yet been completely solved, whilst likewise the problem of high reactivity of lithium, together with the known problems of safety referred to previously, and the problem of reversibility still remain open.

Magnesium could be an element usable for overcoming these problems, and in particular as a replacement for lithium.

As reported in the literature, a number of researchers, such as Farrington and Cherng have sought to develop magnesium-based polymeric electrolyte systems for the possible development of magnesium batteries, with, however, somewhat meagre results. The polymeric electrolytes obtained had, in fact, conductivities which, at room temperature, were too high (i.e., with conductivity lower than 10^{-6} siemens/cm) for the production of primary and/or secondary batteries.

Nevertheless, in the patent US44575 Moulton suggests the possibility of making magnesium batteries, without, however, specifying the procedure, in particular

without specifying how to make the anode, cathode and polymeric electrolyte. Polymeric electrolytes doped with magnesium salts are cited, which, when tested, yielded resistivities higher than 10^7 ohm•cm at room temperature; whereas in order to be able to make the batteries it is necessary for the resistivity values to drop below than 10^5 ohm•cm.

The main task of the present invention is to succeed in developing primary (non-rechargeable) batteries and/or secondary (rechargeable) batteries that overcome the problems of reactivity and reversibility typical of lithium-based batteries.

In the framework of the above-mentioned task, a consequent primary purpose is to develop batteries with high-level technical characteristics allied to a reduction in production costs.

Another important purpose is to develop miniaturized and lightweight batteries.

Yet a further purpose is to develop batteries suitable for use in portable digital electronic equipment.

A further important purpose is to arrive at the almost total elimination of environmental impact.

Summary of the Invention

These and other purposes, which will appear more clearly in what follows, are achieved by primary (non-rechargeable) and secondary (rechargeable) batteries that form the object of the present invention, of the type comprising at least one anode, at least one cathode, at least one electrolyte, and current collectors, said batteries being characterized in that at least the anode and optionally also the electrolyte contain magnesium. Also the cathode of the batteries that form the object of the present invention may optionally incorporate magnesium.

The anode included in the present invention is characterized in that it uses magnesium in the various states of oxidation Mg^{n+} ($0 \leq n \leq 2$), optionally combined with metallic magnesium, and the electrolyte, possibly containing magnesium, is characterized in that it comprises any ionic species of magnesium in solvents, including polymeric solvents, that are capable of producing electrolytes having good ionic conductivity and capable of solvation of the said ionic species.

When the cathode contains magnesium, this is a species of magnesium in the state of oxidation $2+$ and may have a substrate of highly conductive inorganic or

organic materials, or else may be intercalated or embedded in highly conductive inorganic or organic materials.

Forming a further object of the present invention are methods for the production of said primary and secondary batteries of the type comprising at least one anode, at least one cathode, at least one electrolyte set between anode and cathode, and electrical-connection collectors, said batteries being characterized in that at least the anode and optionally also the electrolyte and the cathode contain magnesium. Yet another object of the invention is the use of salts of magnesium chloride in the form for the preparation of the electrolyte, and the use of Grignard magnesium as species generating magnesium cations for the electrolyte.

Further characteristics and advantages will emerge more clearly from the ensuing detailed description of the invention, an embodiment of which is illustrated, merely for the purpose of providing a non-limiting example, in the attached plate of drawing.

15 Brief description of the figure

Figure 1 is a schematic sectional view of a battery built according to the present invention, where:

- 10 designates an anode which has the characteristics and is made as is described in detail in what follows;
- 11 designates a cathode which has the characteristics and is made as is described in detail in what follows; and
- 12 designates an electrolyte which has the characteristics and is made as is described in detail in what follows.

Detailed description of the invention

25 Notwithstanding the fact that the attempts referred to above failed to lead to promising results, the present inventors have now surprisingly found that magnesium is an element that can be usefully employed in making primary and secondary batteries.

Following on extensive and ample research, the present inventors have in fact 30 found that, for the purposes of the present invention, i.e., for obtaining primary and secondary batteries with technical performance comparable, if not superior, to that of lithium batteries at present in use or known, reference being made to the

aforementioned Figure, the batteries that form the object of the present invention may be primary and secondary batteries of the type comprising at least one anode, at least one cathode, at least one electrolyte set between anode and cathode, and current collectors, said batteries being characterized in that at least 5 the anode and optionally also the electrolyte contain magnesium.

In the batteries that form the object of the present invention also the cathode may optionally incorporate magnesium.

When the electrolyte or the cathode do not contain magnesium, they are a conventional electrolyte or cathode, and hence are in themselves known, and 10 consequently will not be described further herein.

The primary and secondary batteries that form the object of the present invention may moreover comprise possible dielectric spacers, not illustrated in the Figure.

In particular, the batteries according to the present invention may be made up of:

- An anode 10 characterized in that it comprises magnesium in the various 15 states of oxidation Mg^{n+} ($0 \leq n \leq 2$), optionally combined with metallic magnesium.

In said anode, the magnesium may be included as such or may also have a substrate of highly conductive inorganic or organic materials, or else of highly conductive inorganic or organic materials that are capable of englobing, by intercalation or embedding into their own matrices, magnesium crystallites of 20 reduced dimensions or magnesium monocrystals.

In particular, the anode 10 may consist of metallic magnesium as such, and in this case the magnesium may be used in laminated or sintered form.

In the case, instead, where the magnesium has a substrate of highly conductive materials, these may be inorganic materials chosen from the group made up of 25 metals, for example aluminium, copper, and other equivalent metals, or oxides, alloys, and fabrics made of the same. The said highly conductive substrate materials may also be organic, and also of a polymeric type; in the latter case, they are chosen from among materials such as carbon-fibre fabrics, graphite, or even graphite-based composite materials, or other equivalent materials suitable 30 for the purposes.

Also in the case where intercalation or embedding materials are used for the anode, this may be either organic or inorganic. The intercalation or embedding

materials that may be used for the purposes of the present invention are transition-metal compounds, alkaline-metal compounds, and alkaline earth-metal compounds, as well as non-metal compounds, chosen from among oxides, sulphides, phosphates or phosphides, such as tungsten oxides (W_yO_x), ferric oxides (Fe_yO_x), titanium sulphides (Ti_yS_x), cobalt oxides (Co_yO_x), nickel oxides (Ni_yO_x), manganese oxide (Mn_yO_x), or else other equivalent compounds, or carbon-based materials with intercalation properties and with a highly crystalline structure or an irregular structure, or equivalent materials, or else a material of a polymeric type, such as carbon-based polymers or equivalent polymers that are capable of englobing, by intercalation or embedding into their own matrices, magnesium crystallites of reduced dimensions or magnesium monocrystals.

Furthermore said anode 10 may be optionally oxidized with oxidizing agents such as oxygen gas or peroxide, such as H_2O_2 , or organic peroxides and stabilized by treatment with stabilizing agents such as alkoxides, (e.g. tetra-alkoxy titanium, tetra-alkoxy silanes, trialkoxy aluminium, tetra-alkoxy zirconium, or magnesium dialkoxide, or equivalent compounds).

A cathode 11 characterized in that it contains magnesium species with state of oxidation 2^+ .

In the case where the cathode contains magnesium, the latter may have a substrate of highly conductive inorganic or organic materials, including polymeric materials, or else the magnesium may be intercalated or embedded in inorganic or organic materials. The materials that may be used both in the case where the magnesium has a substrate and in the case where the magnesium is intercalated or embedded are the same as the materials mentioned previously for the anode.

This type of cathode may be used, dispersing the active material in a porous and conductive matrix. This use affords the advantage of improving the electrochemical properties of the batteries.

Also the cathode may be optionally oxidized with the same oxidizing agents. The oxidation of the cathode may be, like the anode, *in situ* and following on its preparation or, unlike the anode, the cathode may be prepared with electrochemically active materials that have been partially oxidized prior to its preparation.

When the cathode 11 does not contain magnesium, it is a conventional cathode and is in itself known; consequently, it is not further described herein. In this case, anyway, the cathode contains electrochemically active materials having a base of metallic mixtures in appropriate proportions in a reduced or oxidized form. For this purpose, as is known from the prior art, materials containing transition metals may be used, such as, but not exclusively, manganese with state of oxidation ranging from 7^+ to 2^+ , and other equivalent metals.

5 - An electrolyte 12 characterized in that it comprises any ionic species of magnesium in solvents, including polymeric solvents, capable of producing electrolytes with good ionic conductivity and capable of solvating said species.

10 The electrolyte according to the present invention comprises, as ionic species of magnesium, magnesium salts or complexes of the general formula $Mg(R)_yX_{2-y}$, with $0 \leq y \leq 2$, having a very low charge/volume ratio.

The radical R may be chosen from the group consisting, for example, of alkyls with 15 C_1-C_7 chains, whilst X may be chosen from among halides, ClO_4^- , $(CF_3)_{1+x}SO_{3-x}^-$, with $0 \leq x \leq 2$, SCN^- , PO_4^{3-} , or chlorides in δ form, or other equivalents.

15 The compounds of the general formula $Mg(R)_yX_{2-y}$, with $0 \leq y \leq 2$, usable for doping the electrolyte, may moreover be preferentially magnesium salts or magnesium complexes with lattice energy lower than 500 kcal/mol.

20 The solvents used for the electrolyte may be of various types, since the essential characteristic required is that they should possess good ionic conductivity and in any case that they should at the same time be able to solvate the magnesium salts or magnesium complexes that have been chosen. For the purpose, they may therefore be liquid solvents or solvents in the solid or viscous state.

25 In the case of liquid solvents, these are chosen from among materials having polar groups which are able to co-ordinate and dissociate the ionic magnesium salts or complexes and which contain oxygen, nitrogen, sulphur and carbon. These solvents may therefore be chosen from among ethers, alcohols, di-alcohols, esters, amines and amides, thioethers, thioalcohols, thioesters, alkyl carbonates and alkyl thiocarbonates, or other equivalents.

30 In the case where the solvent for the electrolyte is solid or viscous, it may be of a polymeric type.

Usable for the purpose are all the polymers or copolymers of the same having different molecular weights, which are capable of solvating magnesium salts or complexes suitable for the purpose. Such polymers and/or copolymers may be chosen from among polyalkylene oxides, polyalkylene glycols, polycarbonates, 5 polyalkyl siloxanes, polyethylene diaminotetra-acetate, or equivalent polymers or copolymers of the same macromolecular frameworks having different molecular weights, also containing, in their chains, hetero-atoms of the oxygen, nitrogen, silicon, and phosphorus types.

Also usable for the purpose are polyphosphazene polymers functionalized with the 10 polymers and/or copolymers mentioned previously.

To provide examples, among polyalkylene oxides, the following may be mentioned: polymethylene oxide, polyethylene oxide, polypropylene oxide and others; among polyalkylene glycols, the following may be mentioned: polymethylene glycols, polyethylene glycols, polypropylene glycols and fluorinated derivatives of the same and others; among polycarbonates, the following may be mentioned: polymethylene carbonates, polyethylene carbonates, and polypropylene carbonates and others; among the polyalkyl siloxanes, the following may be mentioned: polymethyl siloxane, polyethyl siloxane, and polypropyl siloxane and others.

20 Also usable for the purpose are copolymers derived from the polyalkylene oxides and polyalkylene glycols, polycarbonates, polyalkyl siloxanes, polyethylene diaminotetra-acetate; polyalkylene glycols and polycarbonates, polyalkyl siloxanes, polyethylene diaminotetra-acetate; polycarbonates and polyalkyl siloxanes, polyethylene diaminotetra-acetate; polyalkyl siloxanes and polyethylene diaminotetra-acetate such as, as example, polyethylene oxide-polypropylene oxide, polymethylene oxide-polyethylene oxide, and polymethylene oxide-polypropylene oxide; polyethylene oxide-polymethylene carbonate, polypropylene oxide-polyethylene carbonate, and polyethylene oxide- polypropylene carbonate; polyethylene glycol- polymethyl polysiloxane, polyethylene oxide-polymethyl siloxane, and polyethylene oxide- polyethylene diaminotetra-acetate, etc.

30 It is also possible to use for the purpose, for instance, polyphosphazene polymers functionalized with polymers and/or copolymers of the polyethylene-oxide type or

the like having different molecular weights.

The polymers and/or copolymers that may be used for the preparation of the electrolyte may moreover be functionalized with groups that bond or co-ordinate magnesium so as to improve their interaction with the salts or complexes of the latter.

For the purpose of improving the ionic conductivity of the electrolyte, this may also be optionally acidified or alkalinized according to known procedures, which, consequently, will not be described in greater detail herein.

In the case where the electrolyte is acidified, however, the preferential acidifying agents for the electrolyte are compounds with a base of phosphorus, polyphosphates, P_2O_5 , or equivalents of the orthophosphoric-acid type. In the case where the electrolyte is alkalinized, the compounds that may be used are nitrogen-based ones and, in this case, are preferentially amines or ammonia, as well as basic derivatives of sulphur and phosphorus.

Acidification improves the conductivity of the electrolyte, and this process is to be carried out whenever the performance of the electrolyte is not adequate for the application. This process is to be preferred in the case of stabilized electrodes.

Also alkalinization improves the conductivity of the electrolyte and is carried out with the purpose of favouring the electrochemical functioning of the electrodes.

This process is, however, to be preferred in the case where non-stabilized electrodes are used.

- Spacers (not shown in the Figure) consisting of inorganic or organic materials which are permeable to ions and have high dielectric characteristics; these are appropriately functionalized, if necessary, in order to eliminate the polar groups that may be present on the surfaces of the fibres. For the purpose it is possible to use, for example, cellulose, glass-fibre fabrics, organic membranes, or other equivalent materials.

- Current collectors 13, either metallic or non-metallic, with conductive characteristics and with a resistivity of not more than 10 ohm·m for collecting the electrons and for electrical connection of the poles of the battery element. For the purpose, it is possible, for example, to use metals, even in the form of oxides, alloys, and fabrics made of the same, such as aluminium, copper, steel, brass,

etc., or organic materials made of carbon or carbon-fibre fabrics or similar materials.

The method for making the primary and/or secondary batteries according to the present invention envisages at least one of the following steps:

- 5 - preparation of an anode characterized in that it comprises magnesium in the various states of oxidation Mg^{n+} ($0 \leq n \leq 2$), optionally combined with metallic Mg, said anode having a base of metallic magnesium as such; or else of magnesium on a substrate of highly conductive inorganic or organic materials, or in inorganic or organic materials for intercalation or embedding of the magnesium;
- 10 - preparation of a cathode characterized in that it comprises species of magnesium in the state of oxidation 2^+ having a substrate of highly conductive inorganic or organic materials or in inorganic or organic composite materials for intercalation or embedding of the magnesium;
- 15 - preparation of an electrolyte characterized in that it comprises any ionic species of magnesium in solvents that are capable of producing electrolytes having good ionic conductivity and of solvating said species.

The electrolyte may moreover optionally be reinforced with spacers as described previously.

- 20 The above three components are put in contact with one another, the layer of electrolyte 12 being set in between the anode 10 and the cathode 11. The intimate contact between anode 10, electrolyte 12, and cathode 11 may also be obtained by exerting a slight pressure on the ensemble of components at temperatures of between room temperature and approximately 150°C.

To obtain batteries with adequate performance, the same technologies may be adopted as those used for the preparation of the already known lithium batteries.

25 In particular, it is possible to:

- use single-layer or multi-layer button battery technology;
- connect the multi-layer films in parallel (parallel stacking), or else connect the multi-layer films in series (bipolar stacking), for non-folded structures;
- 30 - use flat-roll design technology or jelly-roll design technology, or flat-stack design technology for folded structures.

Described in detail in what follows are the methodologies for the preparation of the

individual components when these contain magnesium, and hence are not conventional and so known, both in terms of characteristics and in terms of production methodologies, to any person skilled in the branch.

A - General methodologies for the preparation of the components

5 A.1 - Preparation of the anode 10

For the purposes of the present invention, three types of anode 10 may be used: a magnesium-based anode having the characteristics already mentioned previously, (i) as such or (ii) on a substrate of highly conductive organic or inorganic materials, or (iii) intercalated or embedded in material for intercalation or embedding of

10 magnesium.

The magnesium as such may be laminated starting from Grignard-grade magnesium, or may be in the form of powder of appropriate grain size, or else in the form of a ribbon of varying length, which is commercially available. In addition, the magnesium may also be sintered.

15 The anode may also consist of magnesium on a substrate of highly conductive organic or inorganic materials, including polymeric materials, as described previously. This type of anode may be prepared by chemical, thermal vapour, electrolytic, or electrochemical deposition methods of magnesium species.

20 The other type of anode 10 is made with intercalation or embedding material for magnesium. Particularly this anode is prepared by suspending, in a solvent such as benzene, toluene, N-N dimethyl acetamide, dimethyl formamide, or tetrahydrofuran or the like, a mixture of polyethylene or polyvinyl chloride, or polyacrylamide, or polyacrylonitrile, or some other, with intercalation material previously extended up to complete homogenization with magnesium. The system

25 is treated until complete and homogeneous distribution of the above described materials in the solvent itself is obtained. The composite film with a base of intercalation or embedding material is then obtained by slow evaporation of the solvent.

Other methods of intercalation, in addition to the ones described previously, for 30 obtaining the anode, may be based on physical methodologies, such as plasma spraying or sputtering of the magnesium into the intercalation or embedding material chosen.

Whatever the type of anode, this may possibly be subsequently oxidized with oxygen gas or peroxide, such as H₂O₂, or organic peroxides. The anode may, moreover, be subjected to a further and possible stabilization treatment. As stabilizing agents may be used alkoxides, such as tetra-alkoxy titanium, tetra-alkoxy silanes, trialkoxy aluminium, tetra-alkoxy zirconium, or magnesium dialkoxide, or other equivalent compounds.

With the above further processes it is possible to obtain an anode that presents better characteristics of stability, reversibility, and exchange currents.

A.2 - Preparation of the cathode 11

The cathode 11 may be prepared either providing a substrate for the magnesium or with a composite having a base of intercalation or embedding material, adopting methodologies that are similar to the ones already described for the anode 10, and which, for this reason, will not be described further herein. The intercalation materials are the same as those usable for the anode and may be, for example, but not exclusively, with a base of carbon, graphite, titanium disulphide (TiS₂), cobalt dioxide (CoO₂), nickel dioxide (NiO₂), manganese dioxide (MnO₂), or other equivalents chosen from among the ones already mentioned previously.

Like the anode, also the cathode may undergo further processes of oxidation *in situ* and following on its preparation, these processes having already been described previously. Unlike the anode, however, the cathode may be prepared with electrochemically active materials that have been partially oxidized prior to the preparation of the cathode.

A.3 - Preparation of the intercalation material

The intercalation material is chosen from among the materials that may be used for this purpose in the anode or in the cathode, and is prepared according to the general procedure described in what follows. The intercalation material is ground in a ball mill until complete structural disorder of the material is achieved. Subsequently, the material is brought into intimate contact with magnesium carbonates or magnesium oxides. The mixture thus obtained, after homogenization and pelletization is brought up to a temperature of approximately 100°C to 400°C for a period of between 1 and 3 hours, and subsequently to a temperature of between 800°C and 1200°C under a inert atmosphere (for

example, an argon atmosphere), and then kept at the temperature range indicated in vacuum conditions for 1 to 5 days.

A.4 - Preparation of the electrolyte 12

The electrolyte 12 according to the present invention may be prepared using solvents, including, but not exclusively, polymeric solvents, capable of solvating any ionic species of magnesium and of producing electrolytes having good ionic conductivity. The electrolyte according to the present invention comprises, as ionic species, magnesium salts or magnesium complexes of the general formula $Mg(R)_yX_{2-y}$, with $0 \leq y \leq 2$, having a very low charge/volume ratio. The radical R may be chosen from the group consisting, for example, of alkyls with C₁-C₇ chains, whilst X may be chosen from among halides, ClO₄, (CF₃)_{1+x}SO_{3-x}, with $0 \leq x \leq 2$, SCN⁻, PO₄³⁻, or chlorides in δ form. The compounds of the general formula $Mg(R)_yX_{2-y}$, with $0 \leq y \leq 2$, usable for doping the electrolyte, may moreover be preferentially magnesium salts or ionic complexes of magnesium with lattice energy lower than 500 kcal/mol.

The preparation is according to the following reaction:

solvent + salt / inorganic complex → electrolyte

The mode of preparation of the electrolyte 12 according to the above reaction can follow three general procedures. The first regards the direct dissolution of the magnesium salt or complex in the liquid solvent or in the melted polymer (when the latter so permits). The second procedure regards the dissolution of the polymer solvent and the magnesium salt or complex in a common solvent to obtain the polymeric film through slow evaporation of the solvent (solvent-casting). The third procedure regards obtaining polymeric electrolytes which can have a high conductivity and which are based on polymeric electrolytes having a high degree of crosslinking. In these circumstances, the polymeric electrolyte, for obvious reasons, must be prepared obtaining solutions of the monomer and of the magnesium salt or complex preliminarily, and carrying out the polymerization reaction subsequently.

The solvents usable for the purpose are all those already mentioned previously, and in particular, to provide an example, any liquid material having polar groups containing oxygen, nitrogen, sulphur, and carbon, which co-ordinate and

- dissociate the ionic magnesium salts or complexes, such as ethers, alcohols, di-alcohols, esters, amines and amides, thioethers, thioalcohols, thioesters, alkyl carbonates and alkyl thiocarbonates, or else polymers and/or copolymers with different molecular weights, polyalkylene oxides, polyalkylene glycols, 5 polycarbonates, polyalkyl siloxanes, polyethylene dianinotetra-acetate, derivatives thereof in which one or more atoms in the chain are substituted with one or more hetero-atoms chosen from among oxygen, nitrogen, silicon, and phosphorus and polyphosphazene polymers functionalized with the polymers or copolymers mentioned previously.
- 10 Among the magnesium salts or complexes that may be used for the purposes of the present invention, particularly advantageous is $\delta\text{-MgCl}_2$, which, since it has a very low lattice energy, i.e., close to 0 kcal/mol., may be solubilized in organic solvents that are capable of co-ordinating the magnesium, and Grignard magnesium as species generating cations for the electrolyte.
- 15 The electrolyte obtained according to one of the processes described above may also be acidified or alkalinized with the use of procedures and means known for the purpose. In the case where the electrolyte is acidified, it may be preferential for the purposes of the present invention to add appropriate amounts of phosphorus-based compounds, such as P_2O_5 , or other equivalents, under stirring and up to 20 complete dissolution. A similar procedure is followed in the case where the electrolyte is alkalinized with nitrogen-based compounds or with basic derivatives of sulphur and phosphorus.
- A.5 - Preparation of the dielectric spacers**
- The dielectric spacers may be made of any ion-permeable insulating materials having good characteristics of insulating strength and dielectric constant. In the case where the material has polar groups on its surface, chemical inertization is performed by means of appropriate functionalization to prevent interaction with the magnesium ions or with ionic complexes of magnesium. In the case of glass fibres, for example, the hydroxyl groups present on the surface are de-activated by reaction with triethoxyalkyl silane, thus rendering the surface of the spacer highly apolar.
- B - General examples for the production of the components**

The invention is hereinafter further clarified in its general aspects and through a few examples of practical implementation, which have the sole purpose of illustrating the invention without limiting the scope thereof in any way.

B.1 - Example of preparation of the anode 10 by sintering

5 The anode 10 is prepared starting from metallic magnesium which is finely ground and sintered applying a pressure of 1400 MPa. In this way, after applying the pressure for approximately 10 minutes, a metallic film is obtained having the desired thickness.

B.2 - Preparation of graphite thermally pre-intercalated with magnesium

10 A mixture of magnesium oxide and graphite, in a weight ratio ca. of 3% is rendered disordered using a ball mill. This mechanical mixing proceeds for approximately thirty minutes and has the purpose of intimately homogenizing the two components. The mechanical action of the mill moreover increases the crystallographic disorder of the graphite. The material thus obtained is next 15 introduced into a quartz tube and subjected to six nitrogen-vacuum cycles to eliminate any traces of air. Subsequently, the tube is subjected to a vacuum by means of a diffusion pump at a pressure of 10^{-6} mbar and brought up to a temperature of 700°C, at which it is kept for approximately 14 hours.

20 *B.3 - Preparation of the composite cathode 11*

The intercalated graphite, referred to in Example B.2, is suspended in a xylene solution containing, dissolved therein, 10 wt% of polyethylene. From the mixture thus obtained the solvent is made to evaporate slowly (solvent-casting method) to obtain a black, slightly gummy film, which is broken up into tiny flakes and 25 subsequently converted into a sintered cathode 11 by application of a pressure of 1400 MPa.

B.4 - Examples of preparation of the polymers for the electrolyte

Example B.4.1

Commercially available polyethylene glycols with molecular weights from 200 up to 30 1000 may be used.

Example B.4.2

For the preparation of the polymer, it is possible to use commercially available

polymers, such as polycarbonates, or equivalent ones.

Example B.4.3 - (Synthesis of polyethylene glycol-polydimethyl polysiloxane copolymers)

An aliquot of approximately 3 grams of dimethyl dichlorosilane is made to react in 5 toluene with 50 mol% of polyethylene glycol 400. The reaction is conducted in nitrogen for approximately 10 hours. A transparent polymer is obtained having a high viscosity. After eliminating the toluene and the residue of dimethyl dichlorosilane in vacuum conditions (10^{-3} bar) at a temperature of approximately 120°C, a thick liquid polymer is obtained that resembles honey in appearance. The 10 analyses have shown that the material thus synthesized is a copolymer with blocks of polyethylene oxide and polydimethyl siloxane.

Example B.4.4 - (Synthesis of the di-anhydride monomer of ethylene-diaminotetra-acetate acid)

Approximately 3 grams of ethylene-diaminotetra-acetate acid are made to react in toluene with acetic anhydride in the presence of small amounts of pyridine. After 15 approximately two hours of refluxing, the white precipitate of the anhydride of the ethylene-diaminotetra-acetate acid is first filtered and then washed with toluene in a rigorously inert nitrogen atmosphere. The white solid thus obtained is subsequently vacuum-dried for approximately one day. The analyses have shown that the product is the anhydride of pure ethylene-diaminotetra-acetate acid.

Example B.4.5 - (Synthesis of copolymer with blocks of ethylene-diaminotetra-acetate - polyethylene glycol)

The anhydride of the ethylene-diaminotetra-acetate acid is made to react with a 1:1 aliquot of polyethylene glycol having a molecular weight of from 400 to 800.

25 *B. 5 - Example of preparation of δ magnesium chloride*

One gram of metallic magnesium is introduced into a 250-ml flask in a rigorously inert argon atmosphere. The flask is prepared in an argon dry box with reflux drip and vacuum cocks. Approximately 100 ml of *n*-chlorobutane are added to the magnesium using the drip. The mixture thus obtained is made to react for 30 approximately 8 hours under argon flow at the boiling temperature of the chlorobutane. After two hours' reaction, a greyish solid is obtained having a floury appearance. After vacuum-drying for six hours, a white powder is obtained.

Analyses have shown that this is magnesium chloride in δ form.

B.6 - Examples of preparation of magnesium-based polymeric electrolytes

Example B.6.1 - (Preparation of the polymeric electrolyte polyethylene glycol/(MgCl₂)_x)

5 The magnesium salt is previously dissolved in ethyl acetate. In the same solvent, a polyethylene-glycol solution is prepared separately. The two solutions thus obtained are mixed together. After heating for approximately one hour under reflux, the solvent is removed by subjecting it to a vacuum (10⁻³ mbar) and to heating to a temperature of approximately 100°C. Any traces of solvents that are 10 left are subsequently eliminated under high-vacuum conditions (10⁻⁶ mbar) for approximately two days.

Example B.6.2 - (Synthesis of electrolytic polymer polyethylene glycol-poymethilsiloxane)

An amount of polymer polyethylene glycol-poymethilsiloxane is dissolved in ethyl 15 alcohol perfectly anhydrous. Separately in the same solvent is prepared a solution of δ magnesium chloride. Then the two solutions obtained are mixed together, the solvent is subsequently removed under vacuum (10⁻³ mbar) at temperatures from 80° to 100°C.

Example B.6.3 - (Synthesis of the electrolytic polymer obtained by doping the 20 polyethylene-diaminotetra-acetate-polyethereal copolymer with magnesium salts)

The synthesized polyethylene-diaminotetra-acetate-polyethereal copolymer is doped directly with magnesium salts at the melting temperature of the copolymer.

Example B.6.4 - (Direct synthesis, i.e., without solvents, of polymeric electrolytes 25 with a base of polyethylene glycols or polyethylene oxides and δ magnesium chloride)

The polyether polymers of various molecular weights (200 to 200.000) are directly treated with δ -MgCl₂. The heterogeneous system thus obtained is homogenized for complete dissolution of the salt in the polymer by means of heating and continuous stirring.

Example B.6.5. - (Direct synthesis, i.e., without solvents, of polymeric electrolytes 30 having a base of polyethylene glycols or polyethylene oxides and δ magnesium chloride, acidified with P₂O₅)

The polymeric electrolyte obtained according to the foregoing Example B.6.4 is treated with 8 wt% of P₂O₅. The time required for obtaining a polymeric electrolyte by means of stirring and complete dissolution of the P₂O₅ is approximately 4 hours. The addition of P₂O₅ increases the viscosity of the polymer.

5 *B.7 - Example of preparation of the polymeric electrolyte 12 reinforced with glass fibres*

The liquid polymeric electrolyte or solid polymeric electrolyte in the molten state is used for impregnating a glass-fibre fabric. In this way, a thin layer of polymeric electrolyte is obtained which is reinforced with glass fibres.

10 C - Examples of prototypes produced

Practical tests carried out on prototypes revealed that the task and purposes set had been achieved.

In particular, in one first case (single-element button battery with polymeric electrolyte reinforced with a porous paper filter), an anodic disk (anode 10) made of sintered metallic magnesium and having a diameter of 8 mm was interfaced with a film of polymeric electrolyte PEG 400 reinforced with a paper disk having the same diameter, after prior heating of the two compounds. On top of the polymeric-electrolyte film was laid a composite cathodic film (cathode 11) having a base of intercalation material consisting of metal oxides with graphite in liquid suspension subsequently dried, prepared according to the previous examples. The element thus obtained was housed on a system consisting of two current collectors 13. A few instants after assembly, this prototype revealed a voltage of approximately 0.8 V. Within approximately 5-6 hours, the voltage of the battery prototype increased until it reached approximately 1.8 V. After a few rechargings were carried out at a constant current of between 5 and 150 µA, the prototype presented a threshold voltage between 2 and 3 V. After discharge, the voltage returned to 1.8 V.

In a second case (single-element button battery with polymeric electrolyte reinforced with glass fibre), the anode 10 and cathode 11 were prepared according to the same procedures as for the first prototype. In the present case, as reinforcement for the polymeric electrolyte 12, glass fibre having a thickness of 0.02 mm was used. The characteristics of this prototype were the same as for

those of the first prototype, but the reversibility was considerably superior.

In a third case (single-element button battery with polymeric electrolyte acidified with P_2O_5 and reinforced with glass fibres), the anode 10 and cathode 11 were prepared following the same procedures as for the first prototype. Acidification of 5 the polymeric electrolyte 12 by means of P_2O_5 enabled a voltage of approximately 2.2 V to be obtained, together with excellent reversibility, a high specific energy density, and a considerable charge capacity.

From the examples given above there clearly emerge the advantages that may be obtained using magnesium for the production of the batteries that form the object 10 of the present invention. In addition, when compared to lithium, magnesium, which is a very light element, presents characteristics of better workability, together with a good reactivity and oxide-reducing voltage. The possibility for magnesium to exchange two electrons may enable an efficiency of 100%, and, given the same volumes, magnesium may reach 80% more in terms of charge and 45% more in 15 terms of energy as compared to lithium.

The systems developed according to the technology described herein enable, in fact, excellent technical performance to be achieved, allied to the advantage of a reduction in production costs and to the practically total absence of environmental impact, given that the component materials are all non-polluting and that 20 magnesium is a safe element as demonstrated by its medical and clinical uses.

The invention thus conceived may undergo numerous modifications and variations, and, without departing from the scope of the inventive idea of the present invention, it is possible for a person skilled in the branch to make, to the primary (non-rechargeable) and secondary (rechargeable) batteries that form the 25 object of the present invention, all the modifications and improvements resulting from normal technical know-how and experience in the sector, as well as from the natural evolution of the state of the art.

CLAIMS

1. Primary (non-rechargeable) and secondary (rechargeable) batteries, of the type comprising at least one anode, at least one cathode, at least one electrolyte set between anode and cathode, and current collectors, said batteries being characterized in that at least the anode contains magnesium.
2. Batteries according to Claim 1, characterized in that also the cathode contains magnesium.
3. Batteries according to Claim 1, characterized in that also the electrolyte contains magnesium.
4. Batteries according to Claim 1, in which the anode comprises magnesium in the various states of oxidation Mg^{n+} ($0 \leq n \leq 2$), optionally combined with metallic magnesium.
5. Batteries according to Claim 4, in which the anode comprises magnesium in the form of metallic magnesium.
6. Batteries according to Claim 5, in which the metallic magnesium is laminated.
7. Batteries according to Claim 5, in which the metallic magnesium is sintered.
8. Batteries according to Claim 4, in which the anode comprises magnesium on a substrate of highly conductive organic or inorganic material.
9. Batteries according to Claim 8, in which the highly conductive inorganic substrate materials are chosen from among metals, oxides, alloys or fabrics thereof.
10. Batteries according to Claim 8, in which the highly conductive inorganic or organic substrate materials are chosen from among carbon fibre and carbon fibre fabrics, graphite, or graphite-based composites.
11. Batteries according to Claim 4, in which the anode comprises magnesium intercalated or embedded in highly conductive organic or inorganic materials which intercalate or embed, in their own matrices, magnesium crystallites of reduced dimensions or magnesium monocrystals.
12. Batteries according to Claim 11, in which the intercalation or embedding inorganic materials are chosen from among oxides, sulphides, phosphates or phosphides of transition metals, alkaline metals, and alkaline-earth metals, as well as non-metal compounds.

13. Batteries according to Claim 11, in which the intercalation or embedding organic materials have a base of carbons with a highly crystalline or irregular structure.
14. Batteries according to Claim 11, in which the intercalation or embedding 5 organic materials are carbon-based polymers.
15. Batteries according Claims from 4 to 14 in which the anode is oxidised with oxidising agents chosen from among oxygen gas, hydrogen peroxide, or organic peroxides.
16. Batteries according Claims from 4 to 15 in which the anode is stabilized by 10 treatment with alkoxides chosen from among tetra-alkoxy titanium, tetra-alkoxy silanes, trialkoxy aluminium, tetra-alkoxy zirconium, or magnesium dialkoxide.
17. Batteries according to Claim 2, in which the cathode comprises species of magnesium in the state of oxidation 2^+ .
18. Batteries according to Claim 17, in which the cathode comprises magnesium 15 on a substrate of highly conductive organic or inorganic materials.
19. Batteries according to Claim 18, in which the highly conductive inorganic substrate materials are chosen from among metals, oxides, alloys or fabrics made of the same.
20. Batteries according to Claim 18, in which the highly conductive inorganic or 20 organic substrate materials are chosen from among carbon fibre and carbon-fibre fabrics, graphite or graphite-based composites.
21. Batteries according to Claim 17, in which the cathode comprises magnesium in organic or inorganic materials that intercalate or embed magnesium.
22. Batteries according to Claim 21, in which the intercalation or embedding 25 inorganic materials are chosen from among oxides, sulphides, phosphates or phosphides of transition metals, alkaline metals, and alkaline-earth metals, as well as non-metal compounds.
23. Batteries according to Claim 21, in which the intercalation or embedding inorganic or organic materials have a base of carbons with a highly crystalline or 30 irregular structure.
24. Batteries according to Claim 21, in which the intercalation or embedding organic materials are carbon-based polymers.

25. Batteries according Claims from 17 to 24 in which the cathode is oxidised *in situ* with oxidising agents chosen from among oxygen gas, hydrogen peroxide, or organic peroxides.
26. Batteries according Claims from 17 to 24 in which the cathode is prepared with electrochemically active material partially oxidised with oxidising agents chosen from among oxygen gas, hydrogen peroxide, or organic peroxides.
27. Batteries according to Claim 3, in which the electrolyte comprises any ionic species of magnesium in solvents capable of producing electrolytes having good ionic conductivity, and of solvating said species.
- 10 28. Batteries according to Claim 27, in which the electrolyte comprises, as ionic species of magnesium, magnesium salts or complexes having lattice energy lower than 500 kcal/mol.
29. Batteries according to Claim 27, in which the electrolyte comprises, as ionic species of magnesium, magnesium salts or complexes of the general formula $Mg(R)_yX_{2-y}$ ($0 \leq y \leq 2$), where R is chosen from the group consisting of alkyls with C_1-C_7 chains, and X is chosen from among halides, ClO_4^- , $(CF_3)_{1+x}SO_{3-x}^-$ ($0 \leq x \leq 2$), SCN^- , PO_4^{3-} , or chlorides in δ form.
- 15 30. Batteries according to Claim 27, in which the solvent is any liquid material having polar groups containing O, N, S, and C which co-ordinate and dissociate the magnesium salts or complexes.
- 20 31. Batteries according to Claim 30, in which the solvent is chosen from the groups consisting of ethers, alcohols, dialcohols, and esters.
32. Batteries according to Claim 30, in which the solvent is chosen from the groups consisting of amines and amides.
- 25 33. Batteries according to Claim 30, in which the solvent is chosen from the group consisting of thioethers, thioalcohols, and thioesters.
34. Batteries according to Claim 30, in which the solvent is chosen from the group consisting of alkyl carbonates and alkyl thiocarbonates.
35. Batteries according to Claim 27, in which the polymeric solvent is chosen from the group consisting of polymers and/or copolymers with different molecular weights of polyalkylene oxides, polyalkylene glycols, polycarbonates, polyalkyl siloxanes, polyethylene diaminotetra-acetate and their derivatives in which one or

more atoms in the chains are substituted by one or more hetero-atoms chosen from among oxygen, nitrogen, silicon and phosphorus.

36. Batteries according to Claim 27, in which the polymeric solvent is chosen in the group consisting of polyphosphazene polymers functionalized with the 5 polymers or copolymers of claim 35.

37. Batteries according to Claim 35, in which the polyalkylene oxides with different molecular weights are chosen from among polymethylene oxide, polyethylene oxide or polypropylene oxide and the copolymers thereof.

38. Batteries according to Claim 35, in which the polyalkylene glycols having 10 different molecular weights are polymethylene glycols, polyethylene glycols, polypropylene glycols, copolymers thereof and their fluorinated derivatives.

39. Batteries according to Claim 35, in which the polycarbonates having different molecular weights are chosen from among polymethylene carbonates, polyethylene carbonates, or polypropylene carbonates and the copolymers 15 thereof.

40. Batteries according to Claim 35, in which the polyalkyl siloxanes having different molecular weights are chosen from among polymethylsiloxane, polyethylsiloxane, or polypropylsiloxane and the copolymers thereof.

41. Batteries according to Claim 35, in which the copolymers with different 20 molecular weights are between polyalkylene oxides and polyalkylene glycols.

42. Batteries according to Claim 35, in which the copolymers having different molecular weights are between polyalkylene oxides and polycarbonates.

43. Batteries according to Claim 35, in which the copolymers having different molecular weights are between polyalkylene oxides and polyalkyl siloxanes.

44. Batteries according to Claim 35, in which the copolymers having different 25 molecular weights are between polyalkylene oxides and polyethylene diaminotetra-acetate.

45. Batteries according to Claim 35, in which the copolymers with different molecular weights are between polyalkylene glycols and polycarbonates.

46. Batteries according to Claim 35, in which the copolymers with different 30 molecular weights are between polyalkylene glycols and polyalkyl siloxanes.

47. Batteries according to Claim 35, in which the copolymers with different

molecular weights are between polyalkylene glycols and polyethylene diaminotetra-acetate.

48. Batteries according to Claim 35, in which the copolymers with different molecular weights are between polycarbonates and polyalkyl siloxanes.

5 49. Batteries according to Claim 35, in which the copolymers with different molecular weights are between polycarbonates and polyethylene diaminotetra-acetate.

50. Batteries according to Claim 35, in which the copolymers with different molecular weights are between polyalkyl siloxanes and polyethylene diaminotetra-

10 acetate.

51. Batteries according to any of Claims 35-50, in which the polymers and/or copolymers with different molecular weights are functionalized with groups bonding or co-ordinating magnesium salts or complexes.

52. Batteries according to any of Claims 35-51, in which the electrolyte is acidified.

15 53. Batteries according to Claim 52, in which the electrolyte is acidified with compounds having a base of phosphorus, polyphosphates, P_2O_5 , or orthophosphoric acid.

54. Batteries according to any of Claims 35-51, in which the electrolyte is alkalinized.

20 55. Batteries according to Claim 54, in which the electrolyte is alkalinized with compounds being a base or nitrogen such as amines and ammonia, or with basic derivatives of sulphur or phosphorus.

56. Batteries according to Claim 1, in which the current collectors are metallic or non-metallic with a resistivity not exceeding 10 ohm•m.

25 57. Batteries according to Claim 56, in which the metallic current collectors are chosen from the group consisting of metals, oxides, alloys or fabrics made of the same.

58. Batteries according to Claim 56, in which the non-metallic current collectors are made of carbon or carbon-fibre fabrics.

30 59. Batteries according to Claim 1 or 2 or 3, also comprising spacers consisting of ion-permeable inorganic or organic materials having high dielectric characteristics.

60. Batteries according to Claim 59, in which the spacers are chosen from among

cellulose, glass-fibre fabrics, and organic membranes.

61. Batteries according to Claim 59 and Claim 60, in which the spacers are treated so as to eliminate any polar groups present on their surfaces.

62. Use of δ magnesium chloride as ionic species of magnesium for the electrolyte.

63. Use of Grignard magnesium as species generating magnesium cations for the electrolyte.

64. A method for the production of batteries according to Claims 1, characterized in that it envisages of the following step:

10 - preparation of an anode characterised in that it comprises magnesium in the various states of oxidation Mg^{n+} ($0 \leq n \leq 2$), optionally combined with metallic Mg, said anode having a base of metallic magnesium as such, or else of magnesium on a substrate of highly conductive inorganic or organic materials, or in inorganic or organic materials for intercalation or embedding of the magnesium and optionally

15 - preparation of a cathode characterised in that it comprises species of magnesium in the state of oxidation 2^+ having a substrate of highly conductive inorganic or organic materials or in inorganic or organic materials for intercalation or embedding of the magnesium and/or

20 - preparation of an electrolyte characterised in that it comprises any ionic species of magnesium in solvents that are capable of producing electrolytes having good ionic conductivity and of solvating said species.

65. A method for the production of batteries according to Claim 64, in which the anode is made of laminated magnesium.

25 66. A method for the production of batteries according to Claim 64, in which the anode is made of sintered magnesium.

67. A method for the production of batteries according to Claim 64, in which the anode having a base of magnesium on a substrate is prepared by chemical or thermal vapour deposition, or electrolytic deposition, or electrochemical deposition of the magnesium on inorganic materials chosen from among metals, oxides, 30 alloys or fabrics made of the same.

68. A method for the production of batteries according to Claim 64, in which the anode having a base of magnesium on a substrate is prepared by chemical or

thermal vapour deposition, or electrolytic deposition, or electrochemical deposition of the magnesium on inorganic or organic materials chosen from among carbon fibre carbon fibre fabrics, graphite, or graphite-based composites.

69. A method for the production of batteries according to Claim 64, in which the
5 anode with a base of magnesium in intercalation or embedding material is prepared by (i) homogenization and pelletization of a mixture of an intercalation or embedding material, ground up to complete structural disorder, and magnesium carbonates or oxides brought up to a temperature of between 100 and 400°C for a period of time of between 1 and 3 hours, (ii) then heating up to temperatures of
10 between 800 and 1200°C in an inert atmosphere, (iii) and finally keeping at this temperature for 1-5 days in vacuum conditions.

70. A method for the production of batteries according to Claim 64, in which the
15 anode with a base of magnesium in intercalation or embedding material is prepared by solvent-casting of a solvent such as benzene, toluene, N-N dimethyl acetamide, dimethyl formamide, or tetrahydrofuran, containing, in a homogeneous way, a mixture of polymers chosen from among polyethylene, polyvinyl chloride, polyacrylamide or polyacrylonitrile, or similar polymers, and the intercalation or embedding material chosen, previously extended up to complete homogenization with magnesium.

20 71. A method for the production of batteries according to Claim 64, in which the
anode with a base of magnesium in intercalation or embedding material for intercalating or embedding magnesium is prepared by plasma spraying or sputtering of the magnesium into the intercalation or embedding material chosen.

25 72. A method for the production of batteries according any of Claims 65-71, in which the anode is oxidised with oxidising agents chosen from among oxygen gas, hydrogen peroxide, or organic peroxides.

73. A method for the production of batteries according any of Claims 65-72, in which the anode is stabilized by treatment with alkoxides chosen from among tetra-alkoxy titanium, tetra-alkoxy silanes, trialkoxy aluminium, tetra-alkoxy zirconium, or magnesium dialkoxide.

30 74. A method for the production of batteries according to Claim 64, in which the cathode having a base of magnesium on a substrate is prepared by chemical or

thermal vapour deposition, or electrolytic deposition, or electrochemical deposition of the magnesium on inorganic materials chosen from among metals, oxides, alloys, or fabrics made of the same.

75. A method for the production of batteries according to Claim 64, in which the cathode having a base of magnesium on a substrate is prepared by chemical or thermal vapour deposition, or electrolytic deposition, or electrochemical deposition of the magnesium on inorganic or organic materials chosen from among carbon fibre, carbon fibre fabrics, graphite, or graphite-based composites.

5 76. A method for the production of batteries according to Claim 64, in which the cathode with a base of magnesium in intercalation or embedding material is prepared by: (i) homogenization and pelletization of a mixture of an intercalation or embedding material, ground up to complete structural disorder, and magnesium carbonates or oxides brought up to a temperature of between 100 and 400°C for a period of time of between 1 and 3 hours, (ii) then heating up to temperatures of 10 between 800 and 1200°C in an inert atmosphere, (iii) and finally keeping at this 15 temperature for 1-5 days in vacuum conditions.

77. A method for the production of batteries according to Claim 64, in which the cathode with a base of magnesium in intercalation or embedding material is prepared by solvent-casting of a solvent such as benzene, toluene, N-N dimethyl 20 acetamide, dimethyl formamide, or tetrahydrofuran, containing, in a homogeneous way, a mixture of polymers chosen from among polyethylene, polyvinyl chloride, polyacrylamide or polyacrylonitrile, or similar polymers, and the intercalation or embedding material previously extended up to complete homogenization with magnesium.

25 78. A method for the production of batteries according to Claim 64, in which the cathode with a base of magnesium in intercalation or embedding material is prepared by plasma spraying or sputtering of the magnesium into the intercalation or embedding material chosen.

79. A method for the production of batteries according any of Claims 74-78, in 30 which the magnesium of the cathode is oxidized *in situ* with oxidising agents chosen among from oxygen gas, hydrogen peroxide, or organic peroxides.

80. A method for the production of batteries according any of Claims 74-78, in

which the cathode is prepared with electrochemically active materials previously partially oxidized with oxidising agents chosen among from oxygen gas, hydrogen peroxide, or organic peroxides.

81. A method for the production of batteries according to Claim 64, in which the
5 electrolyte is prepared by direct dissolution of the magnesium salt or complex in the liquid solvent or molten polymer.

82. A method for the production of batteries according to Claim 64, in which the electrolyte is prepared by solvent-casting of the common solvent of the polymer and of the magnesium salt or complex.

10 83. A method for the production of batteries according to Claim 64, in which the electrolyte is prepared by dissolution of the magnesium salt or complex in one or more monomers and by subsequent polymerization.

15 84. A method for setting magnesium batteries according to anyone of preceding claims, in which at least one anode, at least one cathode, at least one electrolyte, current collectors and optionally dielectric spacers are put in contact between one another, setting the electrolyte between anode and cathode at temperatures of between room temperature and approximately 150°C.

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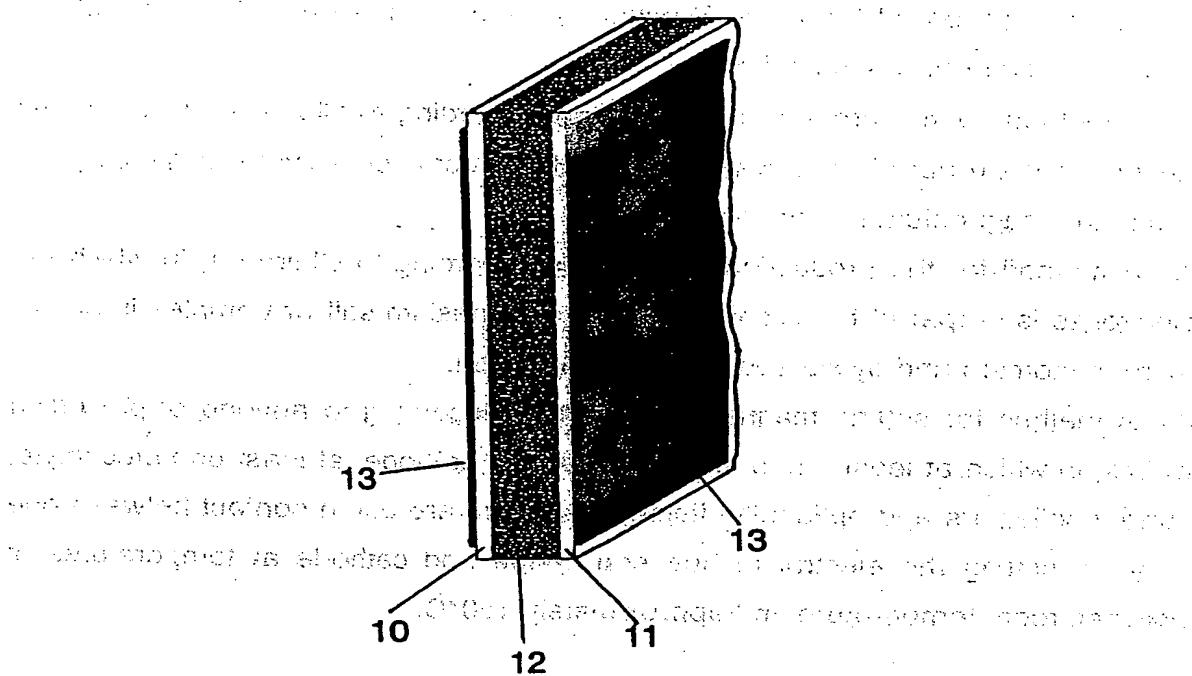


Fig. 1

INTERNATIONAL SEARCH REPORT

Interr Application No

PCT/EP 00/07221

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 H01M10/40 H01M4/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, INSPEC, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>NOTO V D ET AL: "A novel electrolytic complex based on delta-MgCl₂ and poly(ethylene glycol) 400" ELECTROCHIMICA ACTA, GB, ELSEVIER SCIENCE PUBLISHERS, BARKING, vol. 43, no. 10-11, 30 April 1998 (1998-04-30), pages 1225-1237, XP004134179 ISSN: 0013-4686 page 1225, column 1, line 1 -page 1226, column 1, paragraph 2 page 1235, column 2, paragraph 1 -page 1237, column 1, paragraph 1</p> <p style="text-align: center;">-/-</p>	1,27-29, 35,62



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

29 November 2000

Date of mailing of the international search report

12/12/2000

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/07221

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GREGORY T D ET AL: "NONAQUEOUS ELECTROCHEMISTRY OF MAGNESIUM. APPLICATIONS TO ENERGY STORAGE" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, US, ELECTROCHEMICAL SOCIETY, MANCHESTER, NEW HAMPSHIRE, vol. 137, no. 3, 1 March 1990 (1990-03-01), pages 775-780, XP000237613 ISSN: 0013-4651 page 776, column 2, paragraph 3 -page 780, column 2, line 2 ---	1-3, 17, 21, 22, 27-29, 63
X	LIEBENOW C: "A novel type of magnesium ion conducting polymer electrolyte" ELECTROCHIMICA ACTA, GB, ELSEVIER SCIENCE PUBLISHERS, BARKING, vol. 43, no. 10-11, 1998, pages 1253-1256, XP004120633 ISSN: 0013-4686 the whole document ---	1, 3-5, 27-29, 35, 37, 63
X	US 4 894 302 A (HOFFMAN RONALD J ET AL) 16 January 1990 (1990-01-16) column 4, line 18 -column 8, line 44; claims 1-11 ---	1-6, 17, 21, 22, 27, 28, 30, 56, 57, 59, 64, 65
X	EP 0 602 782 A (SANYO ELECTRIC CO) 22 June 1994 (1994-06-22) page 2, line 24 -page 4, line 38 claims 1-5 ---	1-4, 11, 13, 17, 21, 22, 27, 30-34, 56, 57, 59, 60, 64
X	ANDREW PATRICK: "novel solid state polymeric batteries" SOLID STATE IONICS, vol. 18, 1986, pages 1063-1067, XP002153766 page 1063, column 2, line 1 -page 1067, column 2, line 7 ---	1-6, 17, 21, 27, 35 -/-

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/EP 00/07221

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Internat'l Application No
PCT/EP 00/07221

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

International Application No. PCT/EP 00 07221

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-84 in part

Present claims 1-84 relate to an extremely large number of possible primary and secondary batteries only characterized by the presence of magnesium in at least the anode (optionally also in the cathode and/or the electrolyte). Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the batteries claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible.

Furthermore, in view of the large number of claims presently on file, their wording as well as their complex structure of interdependence, which render it difficult, if not impossible, to determine the matter for which protection is sought, the present application fails to comply with the clarity and conciseness requirements of Article 6 PCT (see also Rule 6.1(a) PCT) to such an extent that a meaningful complete search is impossible.

Consequently, the search has been carried out for those parts of the application which do appear to be clear, concise, supported and disclosed, namely for batteries containing magnesium not only in the anode but also in the electrolyte in the form of delta magnesium chloride or Grignard magnesium. This combination is considered to fall within the general definition defined by the features of claims 1,3,4,5,27,29 (where $y>0$) and of independent claims 62,63 and, more specifically, is disclosed and supported by examples B.5 and B.6.1 to B.6.5 of the description on pages 17,18.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/EP 00/07221

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